

Stabilizing Lithium-Metal Anode by Interfacial Layer

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Project ID: bat365

Overview

Timeline

- Start: Oct 1, 2016
- End: Sep 30, 2021
- Percent complete: 70%

Budget

- Total project funding
\$50,000k from DOE
- Funding for FY19
\$10,000k
- Funding for FY20
\$10,000k

Barriers

Barriers of batteries

- High cost (A)
- Low energy density (C)
- Short battery life (E)

Targets: cost-effective and high-energy electrode materials and batteries

Partners

- Collaboration
 - Battery 500 PI's (Jun Liu, Jason Zhang, Jie Xiao, Wu Xu)
 - BMR program PI's
 - Stanford: Prof. Jian Qin, Prof. Michael Toney

Project Objective and Relevance

- Develop lithium-metal based full batteries with 500 Wh/kg specific energy to power electric vehicle and decrease the high cost of batteries.
- Design and fabricate Li metal anodes with high capacity, high coulombic efficiency and long cycle life.
- Design and fabricate novel interfacial layers between lithium metal and electrolytes to overcome the intrinsic material challenges that lead to short battery life, including lithium metal dendrite formation and severe side chemical reactions during electrochemical cycling.

Milestones

FY19

- Q1, Test new Li architectures using B500 protocols (completed)
- Q2, Implement polymer or composite films to demonstrate 20% cycle life improvement with thin lithium (50 um) (completed)
- Q3, Test thin Cu composites current collector using single layer pouch cells (completed)
- Q4 , Quantifying inactive Li using procedures and recipes used by B500 tasks (completed)

FY20

- Q1, Quantifying inactive Li using B500 electrolytes and protocols (completed)
- Q2, Develop new 3D anode structures and test such using coin cell standard protocols to achieve 300-350 Wh/kg (cell-level) for 200 cycles (completed)
- Q3, Develop new polymer protective layers for Li anode, test and report such using coin cell standard protocols (in progress)
- Q4, Select 3D Li architectures and polymer protective layers for pouch cells (single layer and multilayers) (in progress)

Approach

Cell design, fabrication and validation

- 1) Establish cell parameters and requirements for coin cells and pouch cells
- 2) Integrate nanostructured materials in full cells

3D Li metal host anode and interfacial modification

- 1) Design and synthesize Li metal with 3D host composite to overcome volume expansion and contraction problems.
- 2) Design surface modification techniques to generate stable interphase by gas phase reaction and advanced polymer coatings
- 3) Screen electrolytes which can generate stable interface.

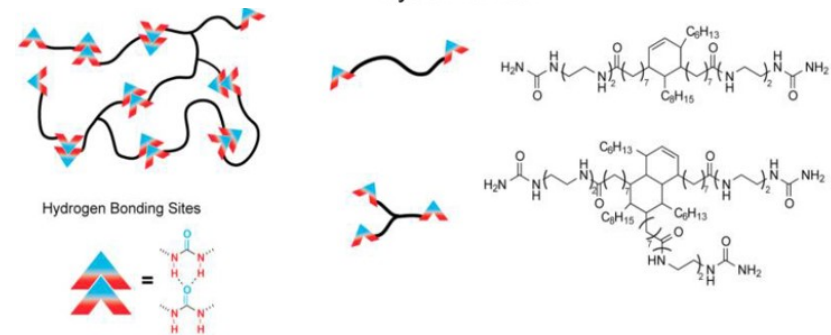
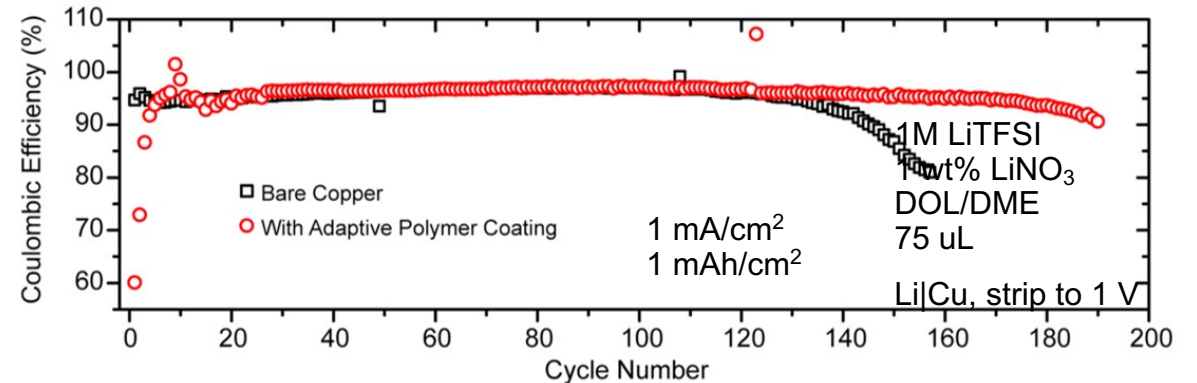
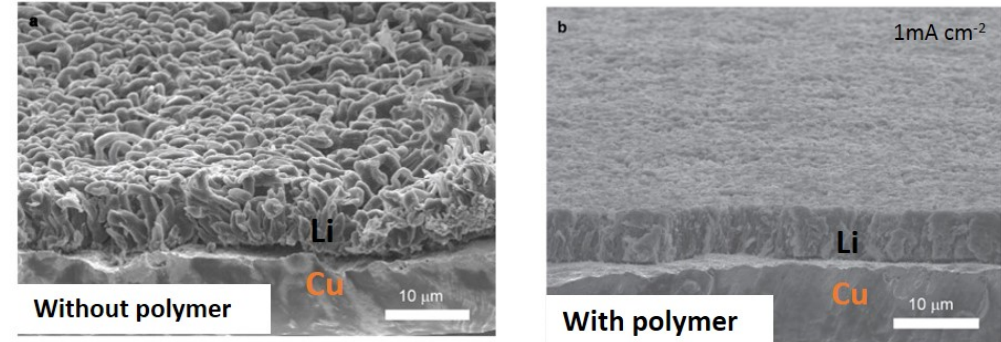
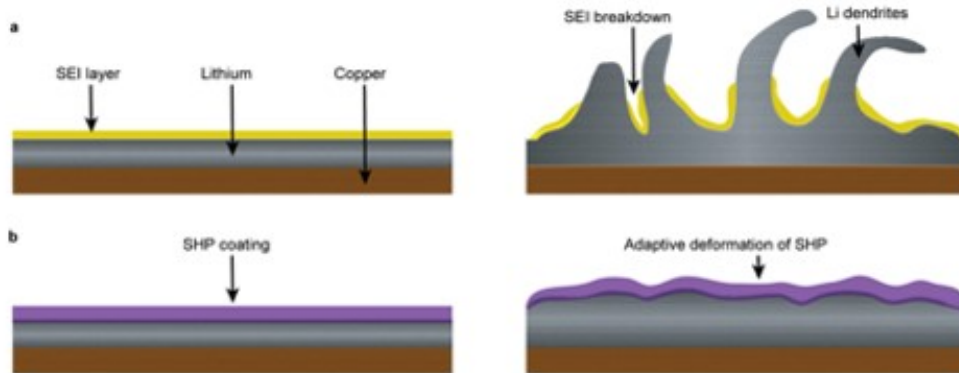
Structure and property characterization

- 1) Transmission electron microscopy
- 2) Cryogenic electron microscopy
- 3) In operando X-ray diffraction and transmission X-ray microscopy

Technical Accomplishments and Progress

#1 Propose Soft Polymer Interface Layer for Li metal

- **Soft, dynamic polymer coating for Lithium – Self-healing polymer (SHP)**
- Viscoelastic supramolecular polymer
- Low glass transition temperature
- Promotes uniform Li deposition



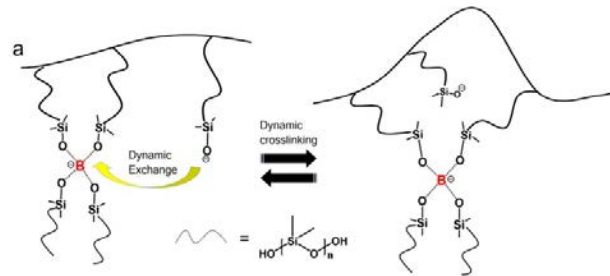
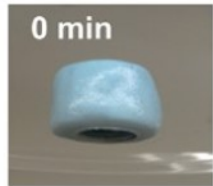
Technical Accomplishments and Progress

#2 Another Soft, dynamic polymer coating for Lithium – “Solid-liquid” hybrid

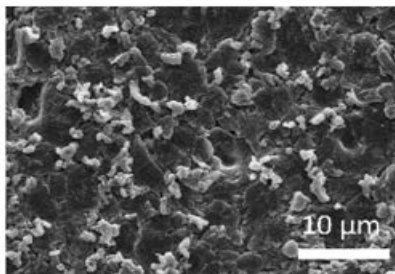
Silly Putty (SP)

- Liquid-like at rest
- Solid-like upon stress

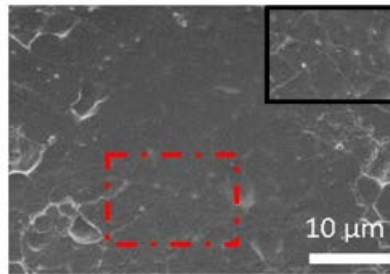
- Dynamic crosslinks enable flowability while providing mechanical stiffness upon dendrite growth.



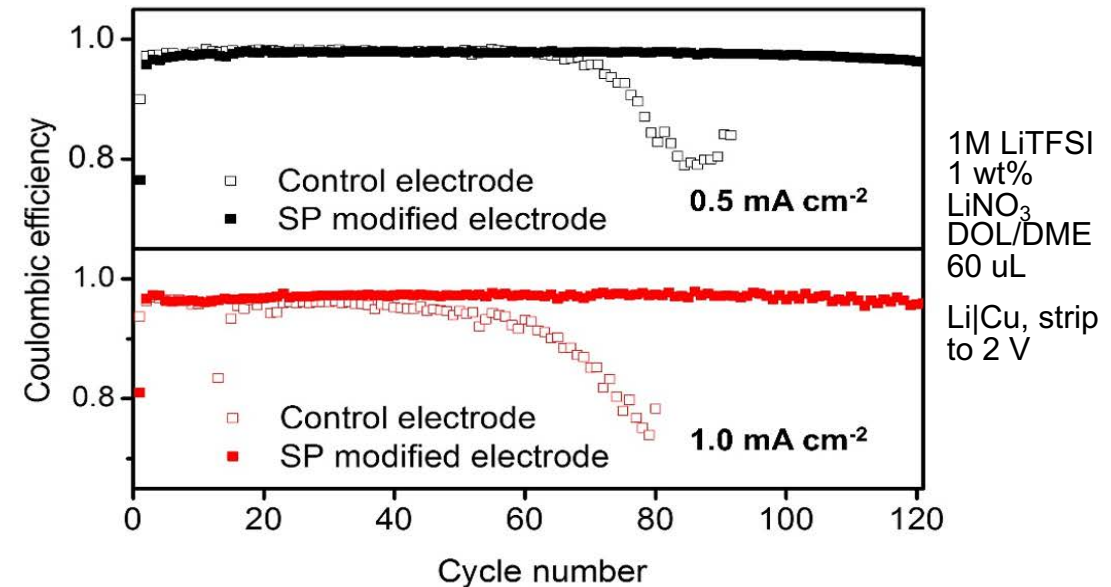
Without SP coating



With SP coating



After 75 cycles

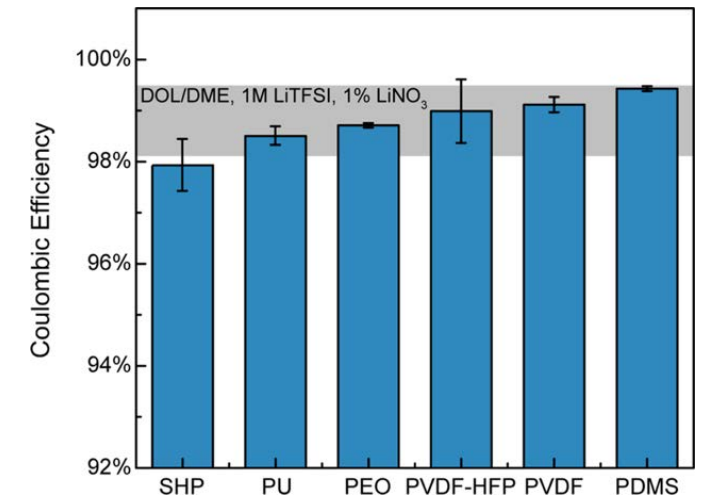
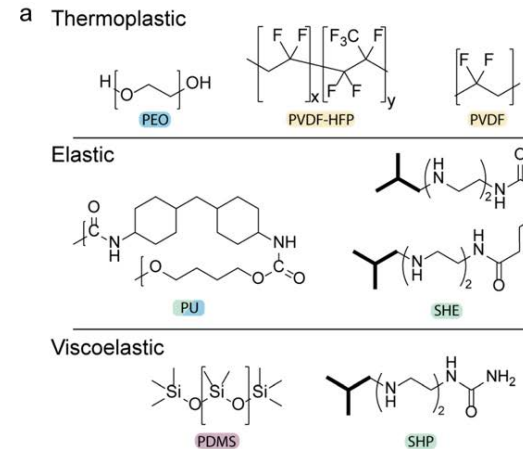
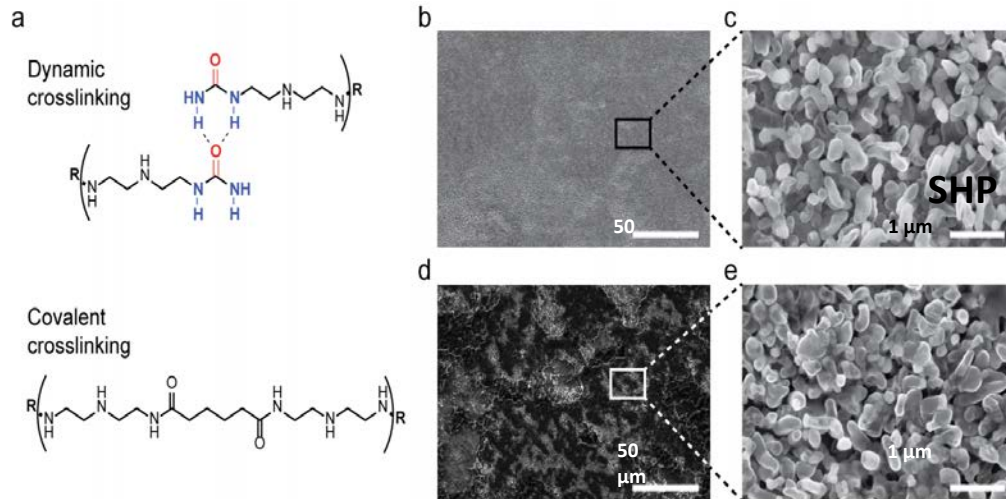


Technical Accomplishments and Progress

#3 Developed understanding of roles of polymer mechanics and polymer chemistry on Li metal deposition

- Polymer mechanics impacts film quality influences deposition uniformity on the electrode scale.

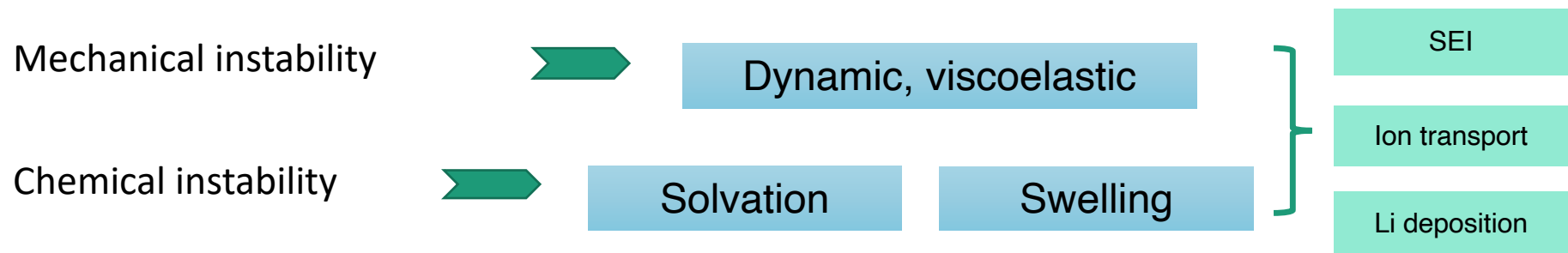
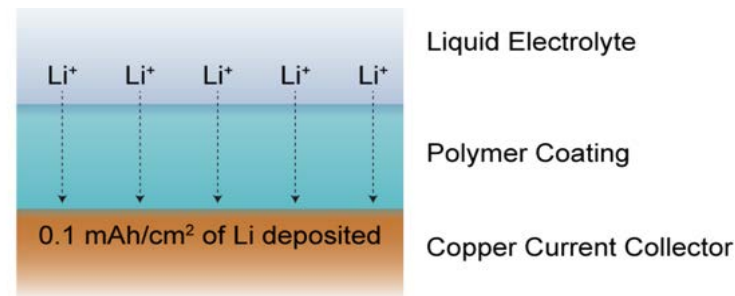
- More Li⁺ solvation/solvent swelling, lower CE



Z. Bao, Y. Cui et al. *J. Am. Chem. Soc.* 2018, 140, 11735–11744

Technical Accomplishments and Progress

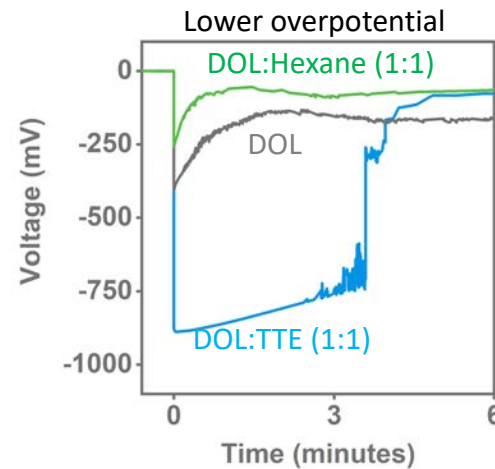
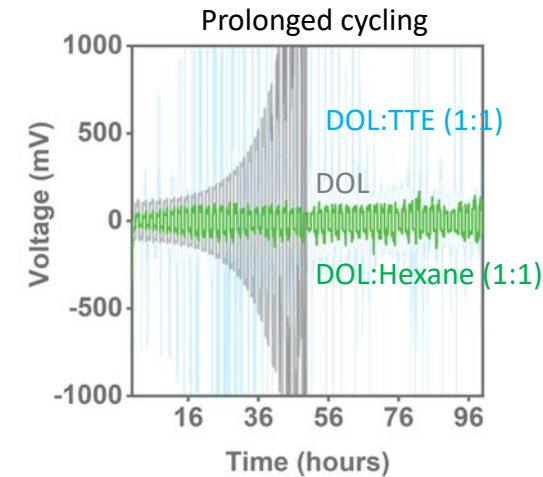
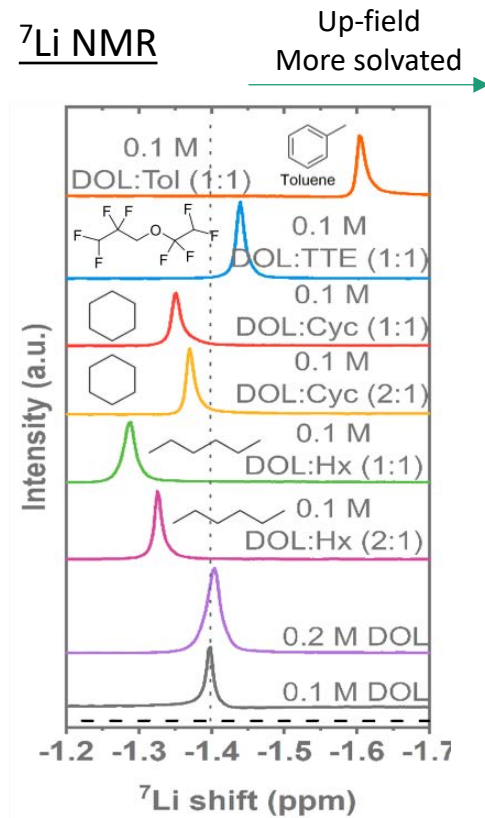
- Propose a clear concept for polymer protective coating
- Mechanical instability of Li metal deposition is addressed by using a dynamic, viscoelastic polymer coating prevents pinholes, non-uniform Li deposition and accommodate volume expansion
- Chemical instability of Li metal deposition is addressed by tuning polymer coating solvation of Li ion and reduce electrolyte solvent swelling



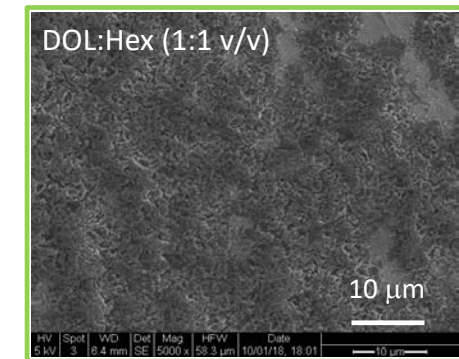
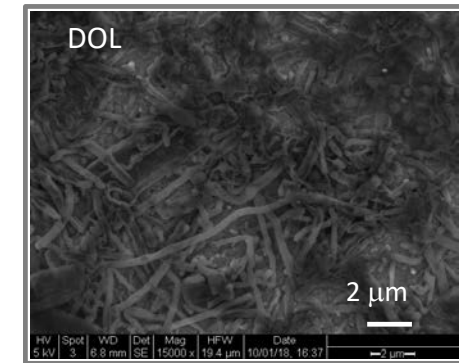
Technical Accomplishments and Progress

- Use model systems to study solvation effect on Li metal deposition
- Less solvated Li⁺ lower overpotential for Li deposition, more plate-like Li growth

0.1M LiTFSI
Capillary
NMR setup
100 μ L
sample in
capillary
1M LiClO₄ in
CD₃CN
deuterated
solv.



Li morphology changed

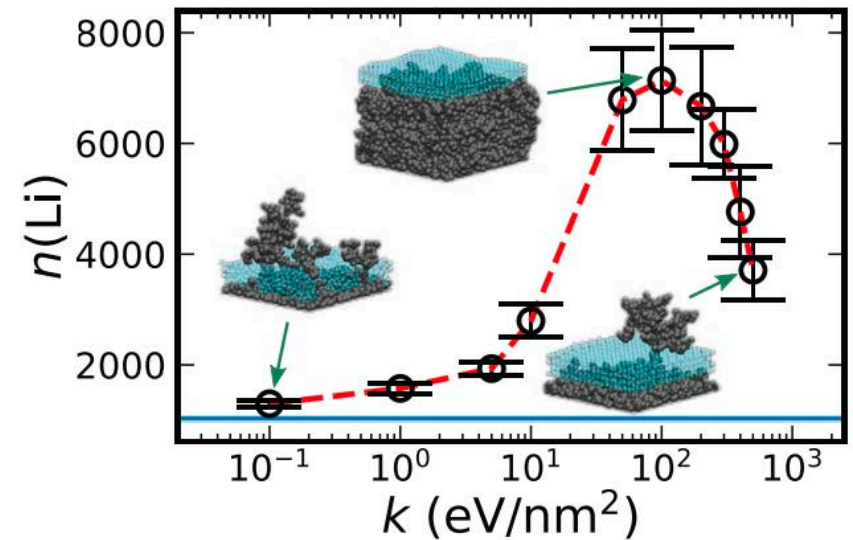
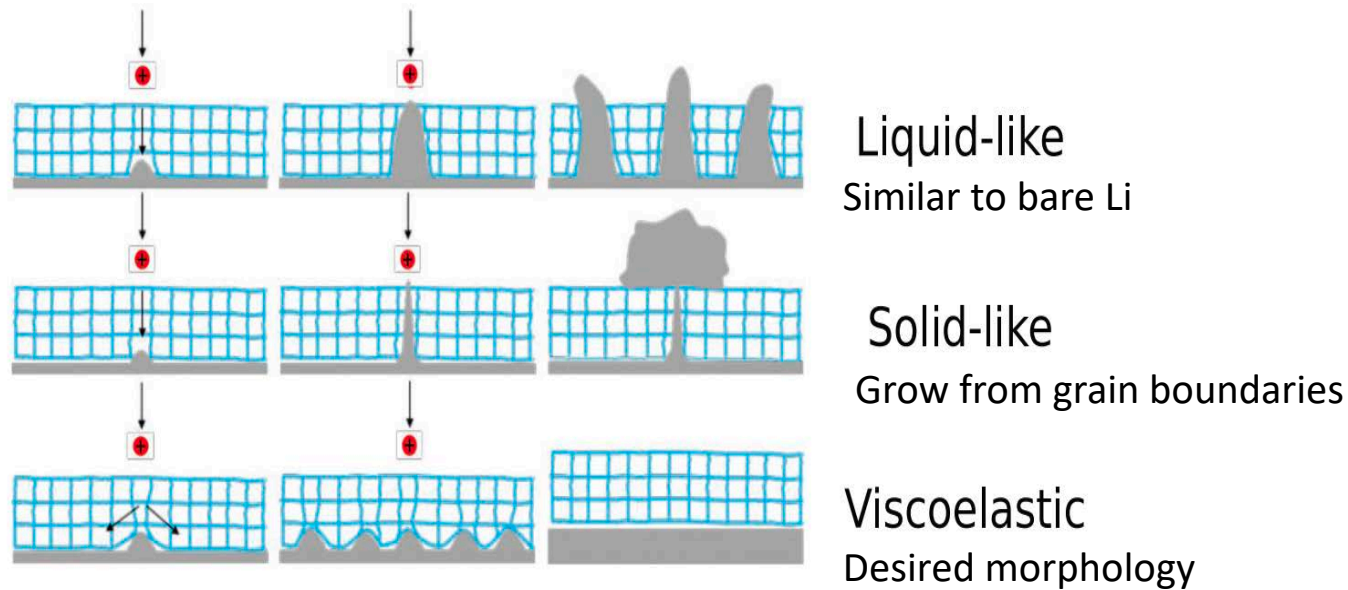


Li/Li

Current rate: 1 mA/cm²
Capacity: 1 mAh/cm²

Technical Accomplishments and Progress

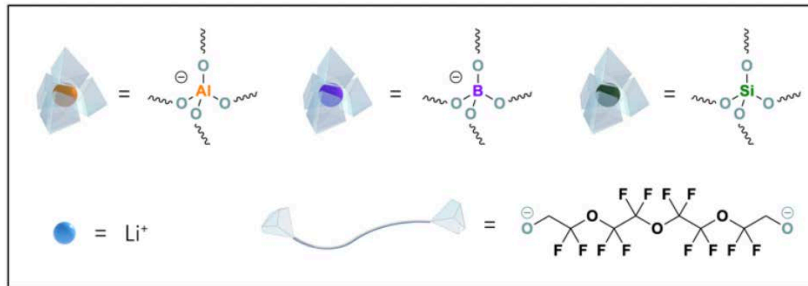
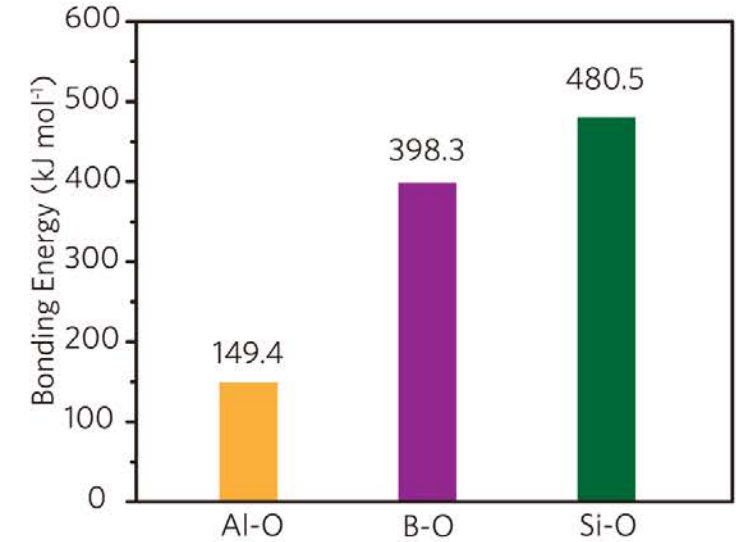
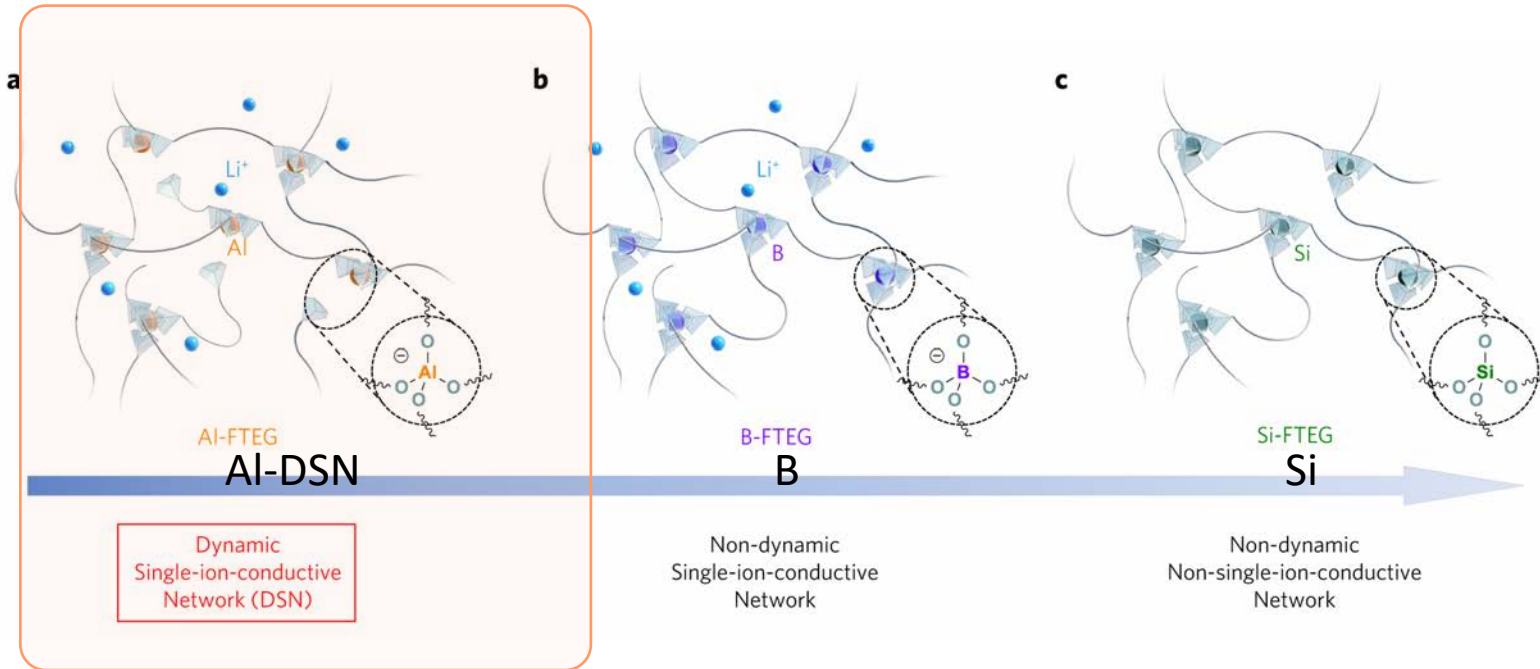
- 3D simulations showed the effect of viscoelasticity on Li deposition
- Viscous polymer gave more uniform Li deposition
- Liquid-like polymer gave dendritic Li growth similar to bare Li
- Solid rigid polymer results in dendrite growth from pinholes



J. Qin, Z. Bao, Y. Cui et al. Adv. Funct. Mater. 2020, 1910138.

Technical Accomplishments and Progress

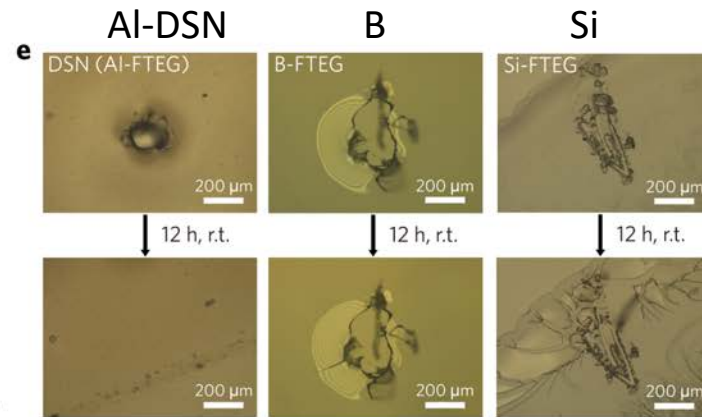
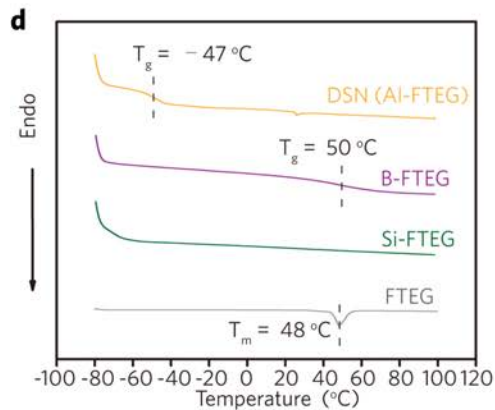
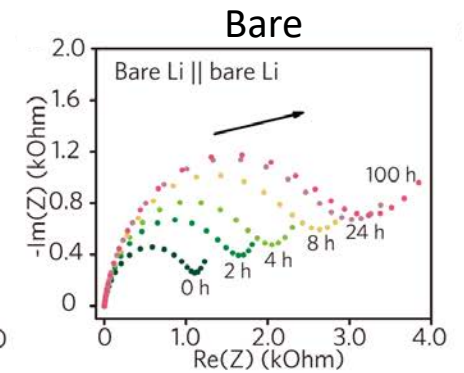
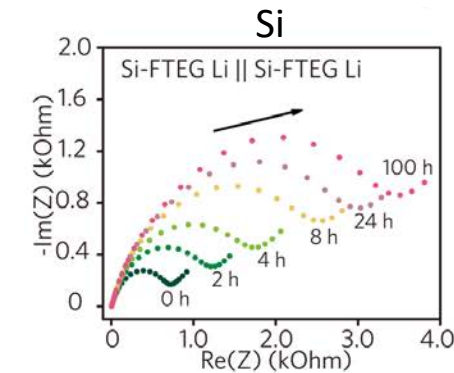
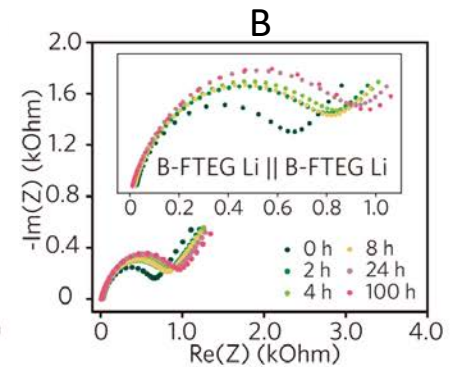
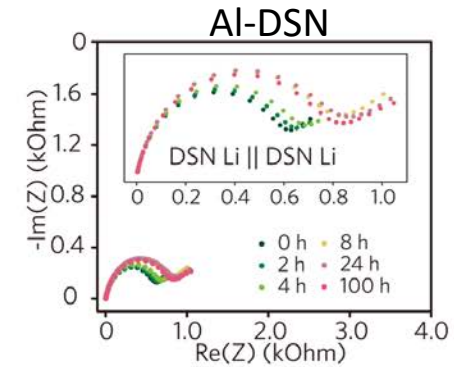
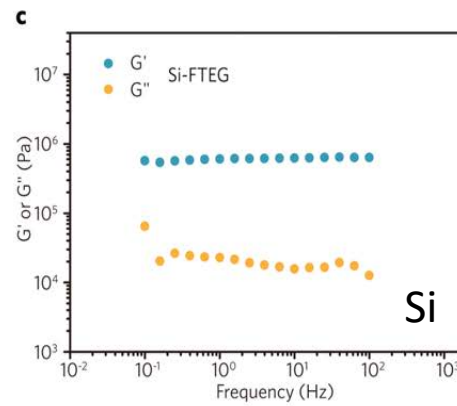
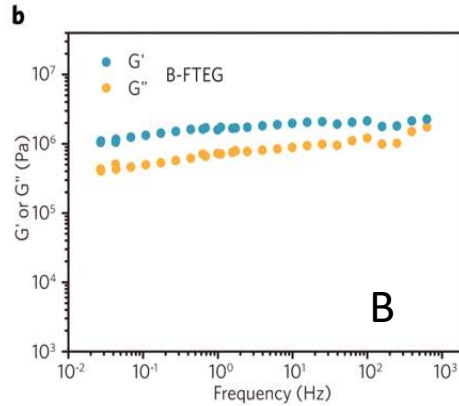
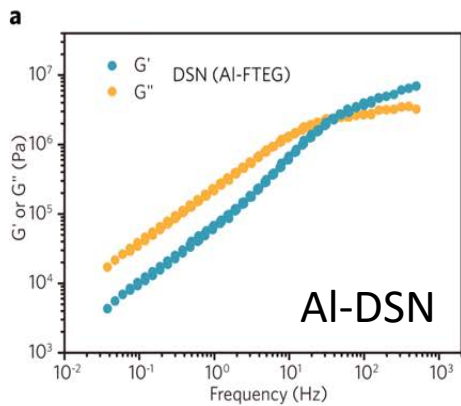
- Artificial SEI design with multifunction in a single matrix



1. Dynamic flowability
2. Fast Li^+ single-ion conduction
3. Electrolyte blocking

Technical Accomplishments and Progress

- Al-DSN show dynamic rheological behavior, B- and Si-FTEG are solid-like
- Al-DSN show self-healing behavior, S- and Si-FTEG are brittle
- Al-DSN has little electrolyte solvent swelling and little impedance change over time



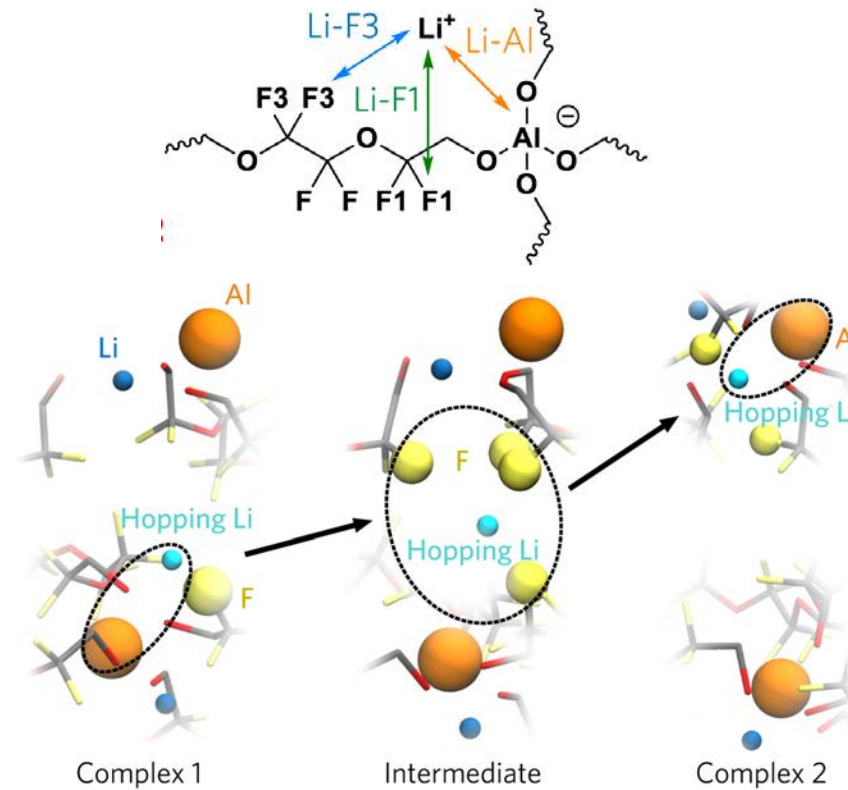
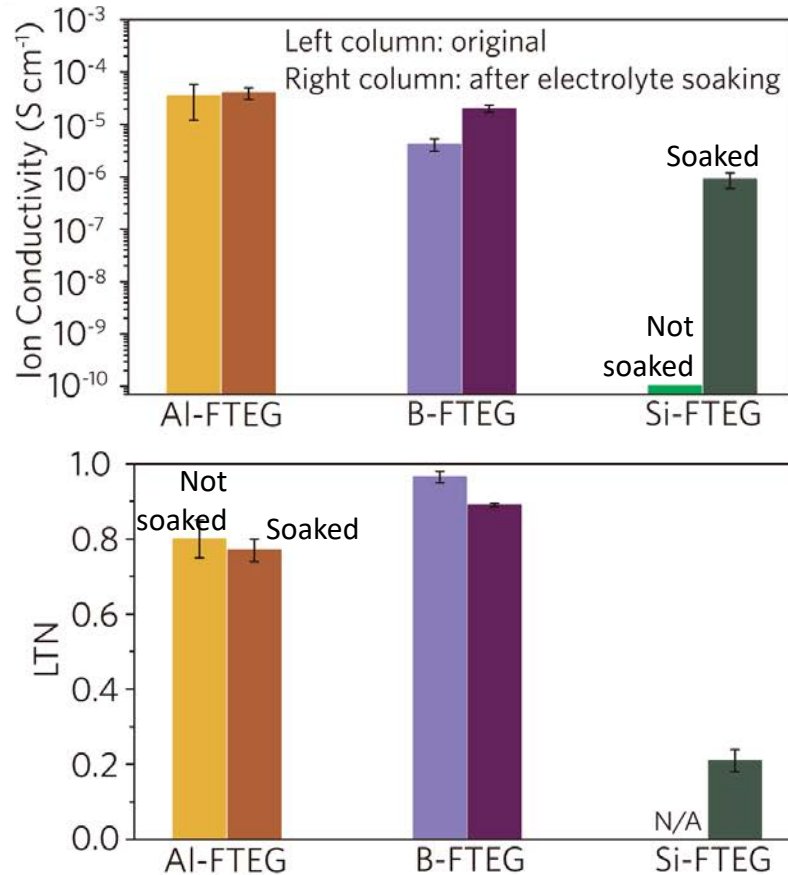
Technical Accomplishments and Progress

- High ion conductivity and transference number with Al-DSN

Al-FTEG: $3.5 \times 10^{-5} \text{ S cm}^{-1}$ and ~ 0.80

B-FTEG: $4.2 \times 10^{-6} \text{ S cm}^{-1}$ and ~ 0.96

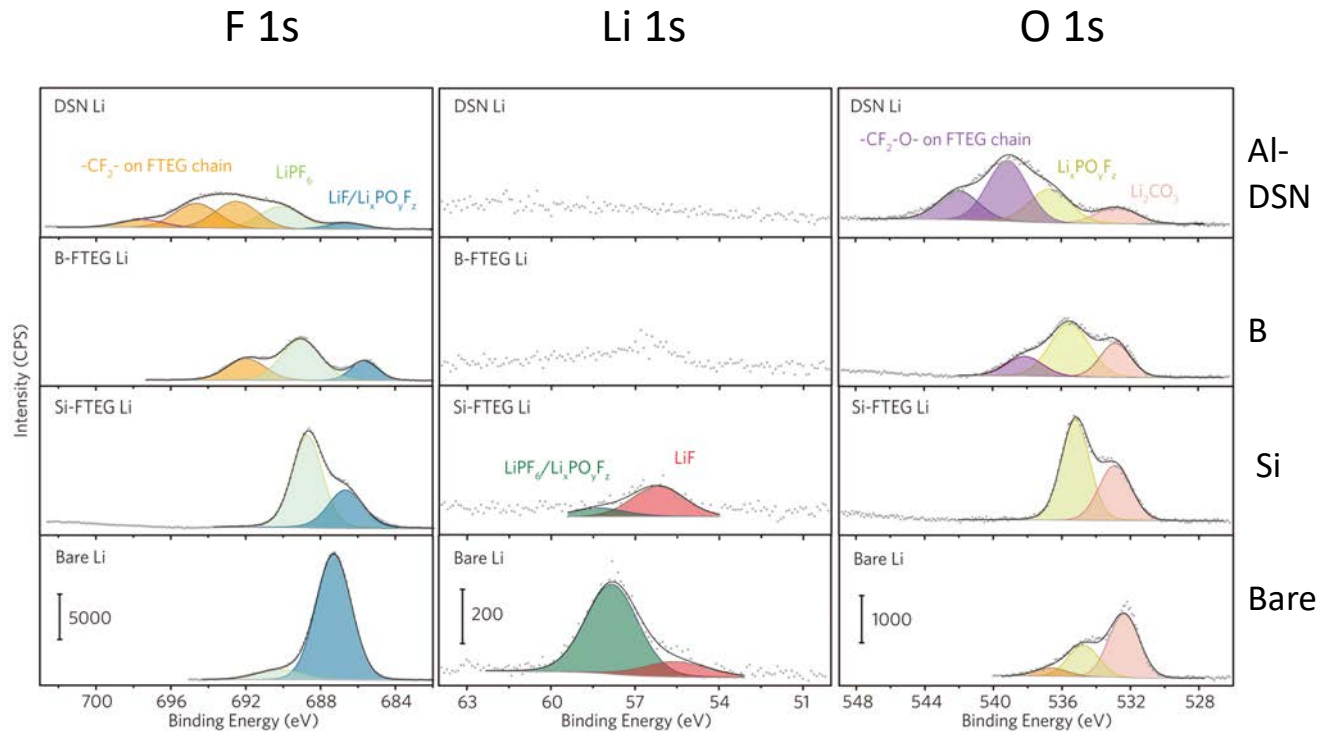
Si-FTEG (w/o Li^+ ions): $< 10^{-10} \text{ S cm}^{-1}$



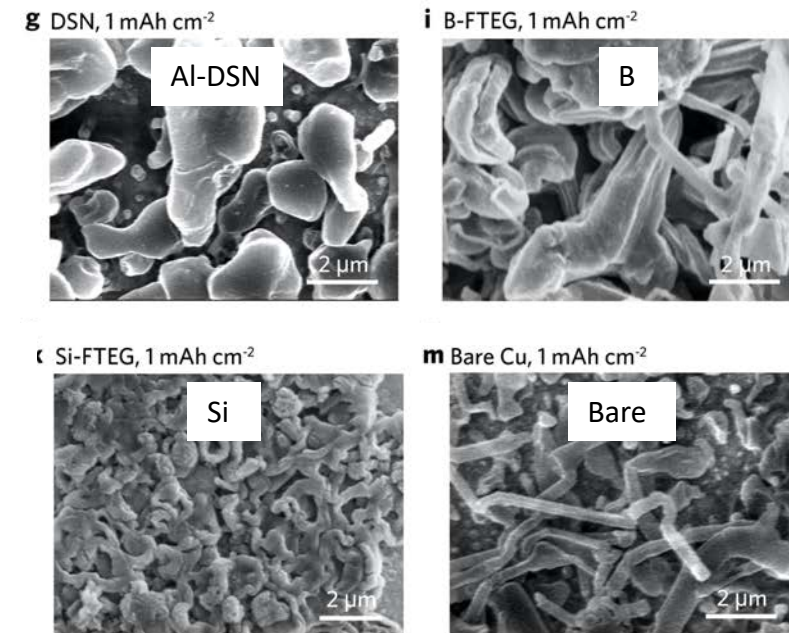
- NMR showed two Li^+ states
- MD simulations showed two RDF peaks and Li^+ transport pathway assisted by F atoms on the chains

Technical Accomplishments and Progress

- XPS: Al-FTEG (DSN): more fluorinated chain but few electrolyte species on the Li surface
 - Desired deposition morphology under Al-FTEG (DSN) and B-FTEG

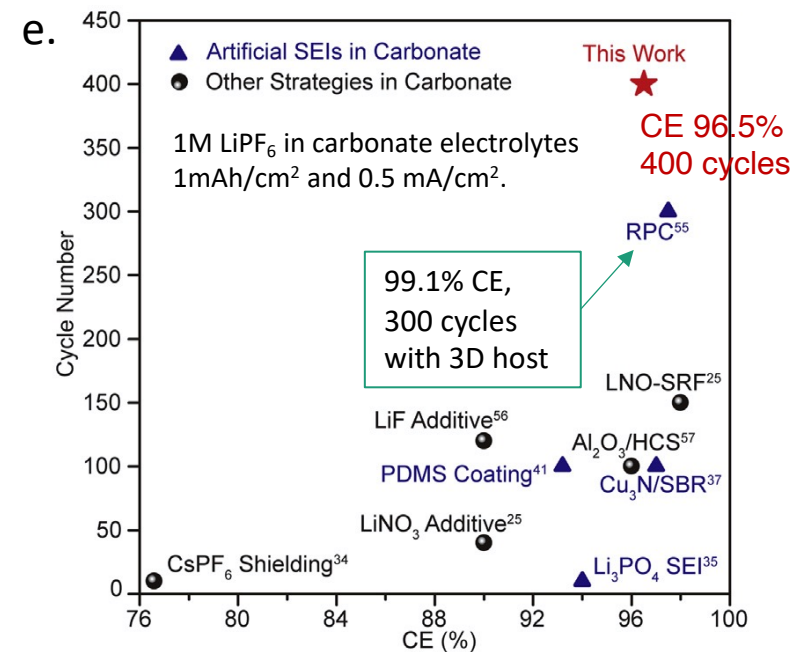
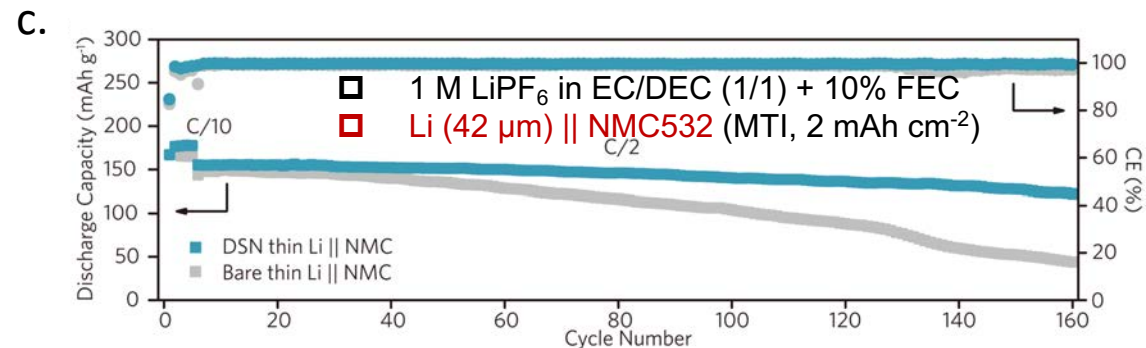
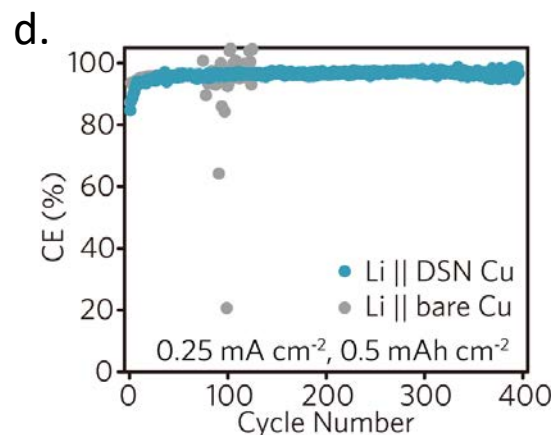
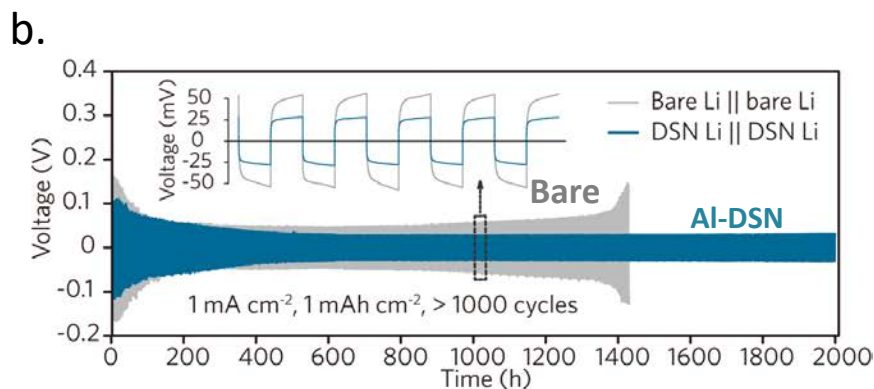
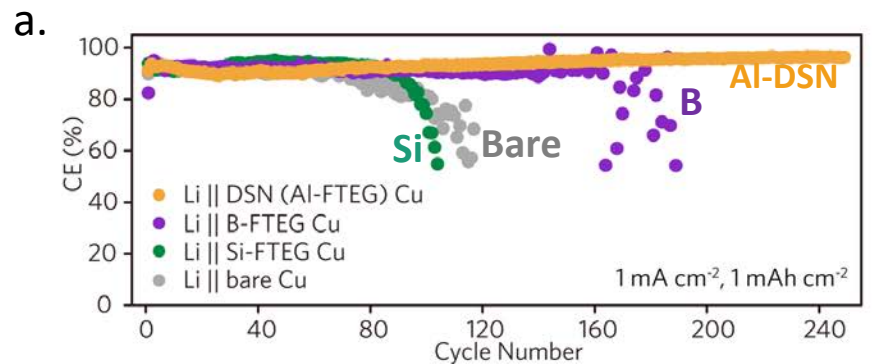


Li deposition morphology



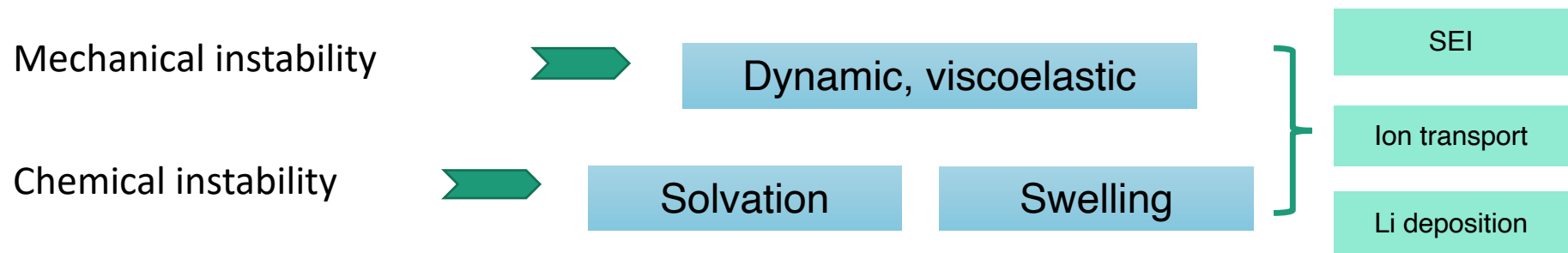
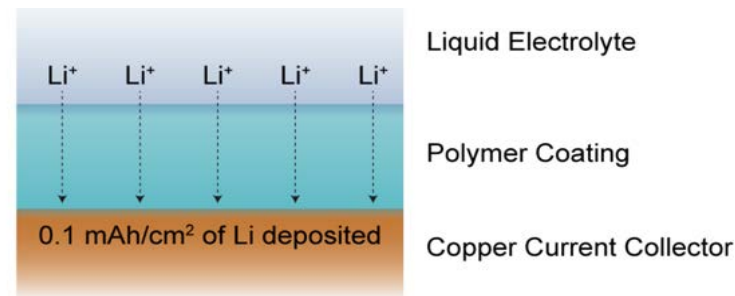
Technical Accomplishments and Progress

- Al-DSN protected Cu showed long Li|Cu half cell cycling
- Thin Li full-cell show 85% retention after 160 cycles



Technical Accomplishments and Progress

- Confirmed concept for polymer protective coating
- Mechanical instability of Li metal deposition is addressed by using a dynamic, viscoelastic polymer coating prevents pinholes, non-uniform Li deposition and accommodate volume expansion
- Chemical instability of Li metal deposition is addressed by tuning polymer coating solvation of Li ion and reduce electrolyte solvent swelling



Responses to Previous Year Reviewers' Comments

None.

Collaboration and Coordination

Battery 500 PI's:

Jun Liu

Jie Xiao

Jason Zhang

Wu Xu

SLAC/ Stanford University:

Prof. Yi Cui

Prof. Jian Qin

Prof. Mike Toney

Remaining Challenges and Barriers

- It is challenging to generate Li metal with high coulombic efficiency and long cycle life to meet the Battery500 goal
- Coulombic efficiency is still not high enough to minimize lithium loss during extended cycles.
- Further designs to be tested to maintain a stable SEI when cycling lithium metal at high areal capacity.

Proposed Future Work

- To further develop artificial SEIs based on rational design rules assisted by simulation and cryoEM study.
- To combine promising artificial SEI with 3D Li host.
- To combine promising artificial SEI with high-performance electrolyte.

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high capacity Li metal anodes and the full battery cells to enable high energy lithium metal-based batteries to power electric vehicles, highly relevant to the VT Program goal.
- **Approach/Strategy:** This project combines advanced polymer design, synthesis, characterization, battery assembly and testing, and guided by simulation and cryogenic electron microscopy study.
- **Technical Accomplishments and Progress:** This project has produced important artificial SEI design rules, meeting milestones. They include identifying the key issues in lithium metal batteries, using rational materials design, synthesis, characterization and simulation. The results have been published in top peer-reviewed scientific journals. The PI and students involved have been recognized by various awards.
- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.
- **Proposed Future Work:** Rational future plan has been proposed.